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Hydrophilicity Difference of TiO$_2$ Thin Films Induced by Different Plasmas

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Abstract

Anatase nanocrystal TiO$_2$ thin films with superhydrophilicity were fabricated by reactive magnetron sputtering metal Ti target followed by thermal annealing in air. The thin films were irradiated with radio frequency (RF) oxygen or nitrogem plasmas with various parameters. Oxygen or nitrogen plasmas irradiation for suitable time with suitable RF power can induce hydrophilicity comparable to photohydrophilicity. The best hydrophilicity was induced by irradiation of the thin films with nitrogen plasma first and followed by oxygen plasma. The irradiated thin films were kept under different light environment to study the light stability. It was found that thin films irradiated with oxygen plasma show highly stable superhydrophilicity whenever kept in dark or under visible light, but for nitrogen plasma-irradiated thin films, the superhydrophilicity deteriorates when kept in dark.

1. Introduction

TiO$_2$ nanoparticle film has good UV photohydrophilicity or UV photocatalysis, which enables it potential applications in self-cleaning and antifogging glass[1]. But at least two factors limit its practical application. Firstly, UV-light comprises only 7 % of the solar spectrum, resulting in low efficiency of photohydrophilicity or photocatalysis of TiO$_2$ thin films under natural light. Secondly, without UV irradiation, the hydrophilicity deteriorates quickly[2]. Finding new way to substitute for UV-light to induce hydrophilicity or catalysis and to maintain its stability are urgent and necessary for promoting its practical applications. Plasma contains electrons, ions, radicals, and neutral molecules. These species interact strongly with surfaces, causing chemical and physical modifications of the surfaces[3]. Plasmas of nitrogen[4] or oxygen[5] were proved to improve the hydrophilicity of TiO$_2$ surface, but the hydrophilicity difference especially the hydrophilicity stability of the irradiated TiO$_2$ thin films has not be reported yet. In this paper, TiO$_2$ thin films were fabricated by direct current (DC) magnetron sputtering metal Ti target and were irradiated by radio frequency (RF) oxygen or/nitrogen plasmas. The relation of hydrophilicity and irradiation parameters were explored. The irradiated sample films were kept in dark or under...
visible light to study the hydrophilicity change with light environment. The best way to keep hydrophilicity stability was suggested.

2 Experimental details

2.1. Fabrication of anatase TiO₂ thin film

Nano- TiO₂ thin films were deposited on glass substrates by DC magnetron sputtering metal Ti target in Ar (5N purity) and O₂ (5N purity) forming gas. Prior to deposition, the chamber was evacuated down to 4×10⁻⁴ Pa. During deposition, the flow ratio of Ar to O₂ is 20:3, and the working gas pressure was kept at 1 Pa by controlling the valve between molecule pump and vacuum chamber. The substrate temperature is about 300°C. After deposition, the films were taken out from vacuum chamber and were put into quartz tube to be annealed under 450°C for 2 hr to form anatase nanocrystal TiO₂.

2.2. Plasma treatments

The plasma treatment was performed using RF- magnetron sputtering system. We arranged a magnetic field under the sample films to increase the ionization probability and the samples were isolated by capacitor to the ground. Once RF power was applied, there will be a negative self-bias voltage formed at the sample. Before irradiation the chamber was pumped down to 5×10⁻⁴ Pa. Then N₂ or O₂ was filled into the chamber, and RF power was applied to generate glow discharge. The TiO₂ films were irradiated by plasma with different parameters.

2.3. Contact angle measurements

The contact angle of water (CAW) was characterized with the diameter of 1 μl water on the surface or with angle degree calculated according to ref [6]. The larger the diameter of 1 μl water, the smaller the CAW.

2.4. Light stability

Nano- TiO₂ thin films irradiated by oxygen or/and nitrogen plasmas were kept in dark or under visible light. 1 hr later the CAW were measured. The light stability was characterized by comparing the CAW just after irradiation with that kept in dark or under visible light for 1 hr.

3 Results and discussion

3.1. Crystalline structure and morphology

The crystalline structure of the samples was characterized by XRD. The XRD pattern of the TiO₂ thin films after annealed was shown in figure 1. The characteristic diffraction peaks of anatase (101), (103), (200), (211), (204) were observed, so the films are pure anatase TiO₂. The morphology of the antase TiO₂ thin film was shown in figure 2. The size of crystal grain is about 20-30 nm.

3.2. UV photon-induced hydrophilicity

Figure 3 shows the evolution of CAW with the irradiation time of 254 nm UV-light. Before irradiation, the CAW is about 14°. Irradiation for 10 s, the CAW begin to decrease, and for 60 s, the CAW reduces to 2°. Three minuter later, the CAW is close to 0°. The film exhibits good photohydrophilicity.

3.3. Oxygen plasma induced hydrophilicity
Figure 4 (a) shows the CAW evolution with RF power of oxygen irradiation. The pressure is 5 Pa and irradiation time is 40s. It shows that high power irradiation increases CAW. We chose 8 W, the lowest RF power, in the following experiment. Figure 4 (b) shows the CAW evolution with irradiation time. The pressure is 5 Pa and irradiation power is 8W. Prolonging the irradiation time, the CAW decreases; reaches a minimum; finally increases (The smaller the diameter of 1 µl water, the larger the CAW).

Figure 1 XRD pattern of TiO\textsubscript{2} thin films after 2hr annealing at 450 °C in air

Figure 2 SEM image of TiO\textsubscript{2} thin film after 2hr annealing at 450 °C in air
3.4. Nitrogen plasma induced hydrophilicity

Figure 5 (a) shows the CAW evolution with RF power. The pressure is 5 Pa and irradiation time is 40 s. It shows that with irradiation power increase, the CAW decreases first and increases after a certain power. This trend is different from that of oxygen plasma case. Figure 5 (b) shows the CAW evolution with irradiation time. From 40s to 9 min, the CAW is really stable, but further irradiation increases the CAW.
3.5. Nitrogen and oxygen plasma induced hydrophilicity

Anatase nano-TiO$_2$ thin films were firstly irradiated by nitrogen plasma RF 8W for 40s and followed by oxygen irradiation with different RF power. Figure 6 (a) shows the CAW evolution with RF power. The pressure of oxygen plasma is 5 Pa and irradiation time is 40 s. It shows that the diameter of 1ul water is larger than that irradiated by nitrogen or oxygen plasma. Figure 6 (b) shows the CAW of nitrogen irradiated films evolve with 8W oxygen plasma for different time. After 15 min irradiation, the diameter of 1ul water reaches 16 mm.
3.6. Light stability

We chose the optimal parameters according to the above experiments to irradiate the nanocrystal TiO$_2$ thin films to study the light stability. After oxygen plasma irradiation, some of the samples were kept in dark and some were kept under visible light. 1 hr later CAW of the films were measured. The results were shown in table 1. Just after irradiation, the CAW is 13 mm, 1hr later, when the sample films were kept in dark or under visible light, the CAW is still 13 mm. The hydrophilicity of the samples are really stable. We conducted same experiment for samples irradiated by nitrogen plasma and the results are also shown in table 1. Just after irradiation, the CAW is 12 mm, 1hr later, for samples kept under visible light, the CAW is 13 mm but for samples in dark it decreases to 8 mm. This experiment indicates that visible light could maintain and even enhance the hydrophilicity of the films irradiated by nitrogen plasma, and when the samples were in dark, some kind of process takes place, which results in the deterioration of hydrophilicity.

<table>
<thead>
<tr>
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<th>Just after irradiation</th>
<th>Under visible light for 1hr</th>
<th>In dark for 1hr</th>
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<tbody>
<tr>
<td>Oxygen plasma</td>
<td>13</td>
<td>13.5</td>
<td>13</td>
</tr>
<tr>
<td>Nitrogen plasma</td>
<td>12</td>
<td>13</td>
<td>8</td>
</tr>
<tr>
<td>Nitrogen-oxygen plasma</td>
<td>14</td>
<td>14.5</td>
<td>11</td>
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It is known that the mechanism for UV induced hydrophilicity is that UV photon produces e-h pair on TiO$_2$ thin film, electrons combine with Ti$^{4+}$ to reduce it into Ti$^{3+}$, and holes oxidize O$^{2-}$ to produce oxygen vacancies in the surface. Water molecules occupy oxygen vacancies, producing absorbed OH group, which tend to make the surface hydrophilic[7]. If no e-h pair supplied, Ti$^{3+}$ will be oxidized into Ti$^{4+}$ and oxygen vacancies may dissapear if there are oxygen available[8]. So hydrophilicity deterioration was observed for most TiO$_2$ films kept in dark[2]. In our irradiation equipment due to the capacitor isolating the sample to the ground, a negative self-bias voltage will be automatically generated, for 8 W, it is about 40V. During irradiation, ions with large energy can implant into the TiO$_2$ films to dope N into the samples[9] and ions with suitable energy can cause sputtering of atoms to generates oxygen vacancies on the surface[10]. When the irradiated samples were kept in dark the surface will be oxidized and oxygen vacancies will disappear[11], which result in the deterioration of hydrophilicity. When the film were kept under visible light, due to N doping, the film can absorb visible light to generate e-h, so the hydrophilicity can be kept.

For oxygen plasmas irradiation, except for implantation and sputtering[12], oxidization[13] takes place. Which one dominating the process depends on the energy of the impinged ions. We made XPS analysis about the samples irradiated at 8 W for 1min, 5 min and 40 W 1 min. It is difficult to fit Ti2p spectra to identify Ti$^{3+}$, but it is easy to fit O2p to determine O in Ti$_2$O$_3$. The details are listed in table 2. According to Ref [14], we attribute O1s at 529.5eV to O in TiO$_2$, O1s at 530.9eV as O in Ti$_2$O$_3$. 40 W plasma irradiates for 1 min increases the ratio of Ti$^{3+}$, while 8W irradiates 5 min decreased the content of Ti$^{3+}$ and increased the content of Ti$^{4+}$, compared with 8 W irradiation for 1 min. It clearly shows oxidization takes place for lower energy irradiation and implantation or sputtering takes place for higher energy irradiation.

<table>
<thead>
<tr>
<th>Sputtering condition</th>
<th>8W 1min</th>
<th>8W 5min</th>
<th>40W 1min</th>
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<tbody>
<tr>
<td>XPS</td>
<td>Peak BE</td>
<td>At. %</td>
<td>Peak BE</td>
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<td></td>
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Table 2

XPS analysis of atom component of TiO$_2$ thin films in different irradiation parameters
Our experiment results indicates that films irradiated by RF 8 W plasma for 1 min shows the best hydrophilicity, but the content of Ti$^{3+}$ is lower than that irradiated by 40 W for 1 min, so except for oxygen vacacies, some other factors are expected responsible for hydrophilicity. According to STM study[15], one oxygen adatom connected to Ti atom will decompose one H$_2$O into two –OH, and it is –OH that was considered directly facilitate hydrophilicity. So we guess the foundament mechanism for hydrophilicity of TiO$_2$ thin film after oxygen plasma irradiation as following. When the surface was irradiated by low RF power plasma, on the one hand, the surface will be sputtered and oxidized. On the other hand, oxygen radicals and neutral molecules may be absorbed on the surface to form adatoms. One absorbed oxygen atom on Ti will decompose one H$_2$O into two –OH, and –OH will combine with H$_2$O to enhance hydrophlicity. After oxygen irradiation, due to the absorbed oxygen on the surface, the surface becomes resistant to oxidation and shows highly stabile superhydrophilicity when exposed to air. That is why the hydrophilicity shows high stability after irradiated by oxygen plasmas.

4 Conclusions

Suitable parameters were chosen to irradiate nanocrystal TiO$_2$ thin films to study the light stability of hydrophilicity induced by plasma irradiation. The hydrophilicity caused by oxygen plasma shows highly stability while the hydrophilicity induced by oxygen plasma irradiation is sensitive to light environment. The best way to obtain highly stable TiO$_2$ thin films is to irradiate the films with nitrogen plasma first and then with oxygen plasma.

Reference